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PROCESS FOR THE REMOVAL OF MERCAPTAN COMPOUNDS FROM PETROLEUM OILS

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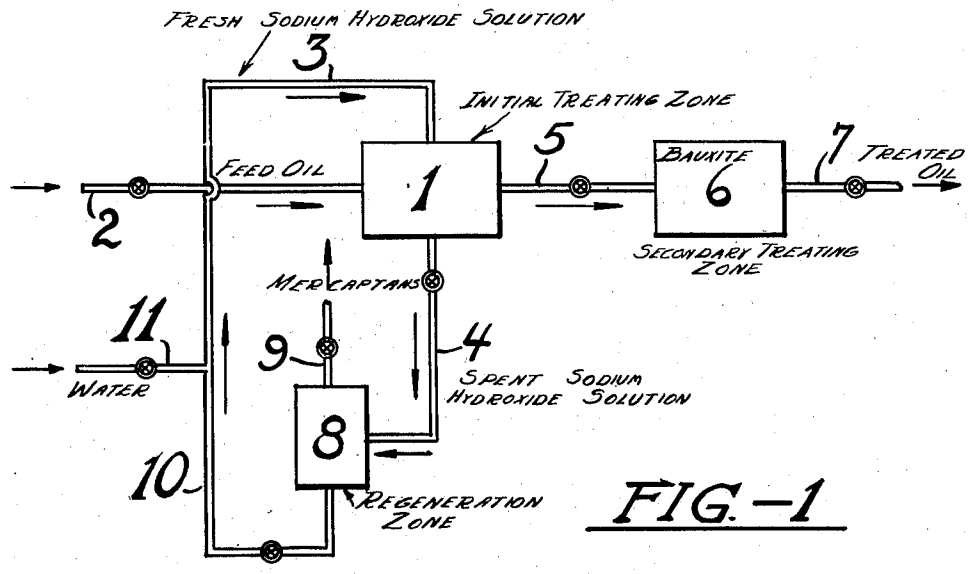


FIG.—1

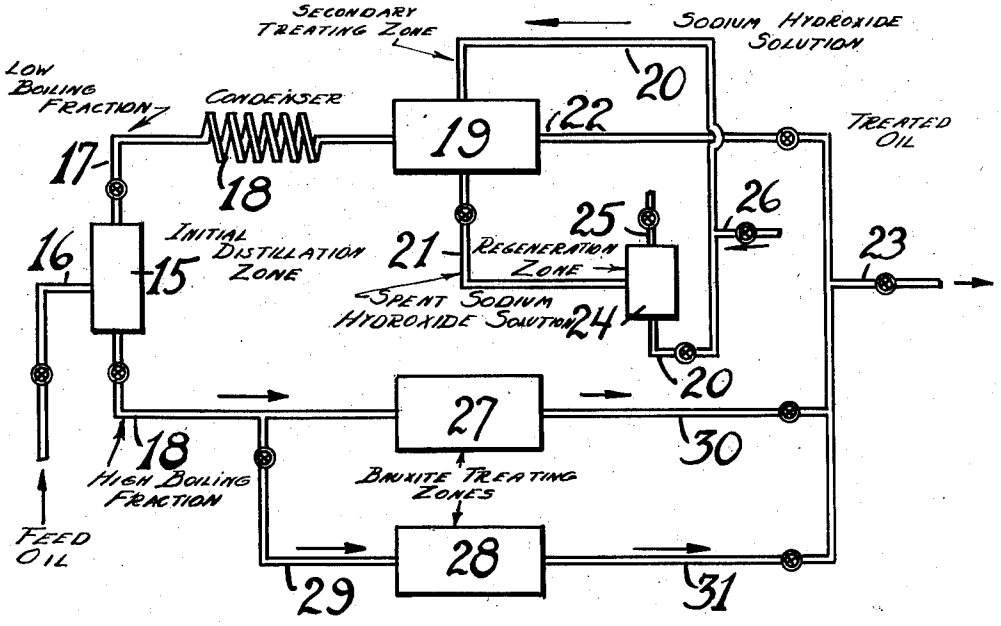


FIG.—2

Amiot P. Hewlett Inventor
By P. L. Young Attorney

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PROCESS FOR THE REMOVAL OF MERCAPTAN COMPOUNDS FROM PETROLEUM OILS

Amiot P. Hewlett, Cranford, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

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3 Claims. (Cl. 196—30)

The present invention relates to the refining of mineral oils. The invention is more particularly concerned with the refining of petroleum oils boiling in the motor fuel, kerosene and gas oil boiling ranges and especially relates to an improved process for the removal of objectionable compounds therefrom, as for example sulfur compounds such as mercaptans. In accordance with the present process these oils are treated in an operation which involves an alkali metal hydroxide treating stage and a bauxite treating stage.

It is well known in the art to refine mineral oils, particularly petroleum oils by various procedures involving distillation, acid treating, clay treating and neutralization stages. For example, it is well known in the art to remove objectionable sulfur and related compounds from petroleum oils particularly from those oils boiling in the motor fuel boiling range by treating the same with mineral acids. The spent acid solution is removed from the oil which is then washed in order to remove free acid constituents. The oil, after removal of the washing solvent is completely neutralized by treating the same with an alkali treating agent such as an aqueous solution of sodium hydroxide. In these operations the mineral acid usually comprises an acid of sulfur such as sulfuric acids of various concentrations. The acid treating operation is usually conducted under conditions to secure a maximum removal of the objectionable sulfur compounds with a minimum degradation of valuable oil constituents. Generally, the operation is conducted at a temperature in the range from about 70° F. to about 80° F. and at atmospheric pressure although lower temperatures may be employed. The mixture after a sufficient time of contact is handled in a manner to remove the spent acid as sludge which contains the objectionable sulfur compound as well as other undesirable constituents. The separated treated oil, which is generally termed "acid oil," substantially free of sulfuric acid is then treated, usually by washing with a washing solvent comprising water, followed by contacting the same with a neutralizing agent such as an alkali metal hydroxide solution as, for example, a sodium hydroxide solution.

Operations of this character have several disadvantages particularly when treating petroleum oils boiling in the motor fuel boiling range. The operation is difficult to control so that the relatively desirable hydrocarbon constituents are not removed from the petroleum oil along with the undesirable mercaptan and related compounds. When these constituents are removed, the treated motor fuel has a relatively low octane number. Furthermore, the operation has the disadvantage that when treating oils boiling in the motor fuel boiling range, it is difficult to remove the final traces of the acid without incurring emulsification difficulties which results in an appreciable loss of the treated oil. In order to overcome these disadvantages, various suggestions have been made for the removal of the undesirable constituents from petroleum oils utilizing other procedures rather than conventional sulfuric acid processes. For example, it has been suggested that petroleum oils such as motor fuels be treated with an alkali solution such as a sodium hydroxide solution in order to remove the objectionable mercaptan and related compounds. This operation while entirely satisfactory for the removal of relatively low boiling mercaptans such as those boiling below about 212° F. to about 225° F. is not effective and cannot be economically used in commercial operations for the removal of relatively high molecular weight mercaptans.

It has also been suggested that petroleum oils be processed by contacting the same with bauxite at various temperatures and pressures. While this operation removes objectionable mercaptan compounds provided a sufficient quantity of bauxite be employed, it has heretofore been impractical to use this process in a commercial operation due to the fact that a prohibitive quantity of bauxite is necessary in order to remove the mercaptan compounds to the desired extent. I have, however, now discovered an operation comprising an alkali metal hydroxide treating stage and a bauxite treating stage by which unexpected desirable results are secured. My invention has been the result of the discovery of the fact that the difficulties involved in the use of the bauxite have been that although the relatively high molecular weight mercaptans are readily removable by the use of bauxite, it is relatively difficult to remove the relatively lower molecular weight mercaptans.

The process of my invention may be readily understood by reference to the attached drawing illustrating modifications of the same. Figure 1 illustrates a modification of my invention in which the feed oil is subjected in an initial stage to treatment with an alkali metal hydroxide solution and the entire quantity subjected in a secondary stage to a treatment with bauxite. Figure 2 illustrates the preferred modification of my invention in which the feed oil in an initial stage is segregated into a relatively low boiling frac-

tion and into a relatively high boiling fraction. The relatively low boiling fraction is contacted in a secondary stage with an alkali metal hydroxide solution while the relatively high boiling fraction is subjected in a tertiary stage to treatment with bauxite.

Referring specifically to Figure 1, it is assumed for the purposes of description that the feed oil comprises a petroleum oil boiling in the motor fuel boiling range which feed oil contains mercaptan compounds boiling over this range. The feed oil is introduced into initial treating zone 1 by means of feed line 2. In initial treating zone 1 the feed oil is treated with an alkali metal hydroxide solution which for the purposes of description is assumed to be a sodium hydroxide solution of about 10° Bé. concentration. The fresh sodium hydroxide solution is introduced into zone 1 by means of line 3 while the spent sodium hydroxide solution is withdrawn by means of line 4. It is to be understood that initial contacting zone 1 may comprises any suitable number and arrangement of stages. The operation may comprise a batch, a semi-batch or a countercurrent treating process. The sodium hydroxide contacted oil is removed from initial treating zone 1 by means of line 5 and passed into secondary treating zone 6 in which the oil is contacted with bauxite. The bauxite treated oil is withdrawn from secondary zone 6 by means of line 7 and further refined or handled in any manner desirable. The spent sodium hydroxide solution is passed to regeneration zone 8 which comprises a distillation unit and handled in a manner to remove overhead the mercaptan compounds by means of line 9. The regenerated sodium hydroxide is withdrawn from distillation zone 8 by means of line 10 and recycled to initial contacting zone 1. The concentration of the sodium hydroxide solution may be adjusted to the desired degree by introducing additional water by means of line 11 to compensate for the water removed overhead in distillation zone 8.

Referring specifically to Figure 2, it is assumed that the feed oil is similar to the feed oil described with respect to Figure 1. The feed oil is introduced into initial distillation zone 15 by means of line 16. Temperature and pressure conditions are adjusted to remove overhead by means of line 17 a relatively low boiling fraction which for the purposes of description is assumed to boil in the boiling range from about 100° F. to about 212° F. A relatively high boiling fraction boiling in the range from about 212° F. to about 400° F. is withdrawn as a bottoms from distillation zone 15 by means of line 18. The relatively low boiling fraction is condensed in condenser 18 and introduced into secondary treating zone 19 in which it is contacted with an alkali metal hydroxide solution which for the purposes of description is assumed to be a sodium hydroxide solution. The fresh sodium hydroxide solution is introduced into secondary zone 19 by means of line 20 and while the spent sodium hydroxide solution is withdrawn by means of line 21. The treated oil is removed from secondary zone 19 by means of line 22 and withdrawn from the system by means of line 23 and further refined or handled in any manner desirable. The spent sodium hydroxide solution withdrawn by means of line 21 is introduced into regeneration zone 24 which for the purposes of description is assumed to be a distillation zone. Temperature and pressure conditions are adjusted to remove overhead by means of line 25 the mercaptan compounds. The regenerated sodium hydroxide is withdrawn by means of line 20 and recycled to secondary treating zone 19. The concentration of the sodium hydroxide solution may be controlled by introducing water by means of line 26 in order to compensate for the water lost in the distillation zone. The relatively high boiling fraction removed by means of line 18 is introduced into the bauxite treating zone which for the purposes of description is shown to comprise bauxite treating units 27 and 28. These units operate in a manner so that while the oil is contacting bauxite in one unit, the bauxite in the other unit is being regenerated. The oil is introduced into bauxite units 27 and 28 by means of lines 18 and 29 and withdrawn from the respective units by means of lines 30 and 31. The bauxite treated oil is combined with the relatively low boiling sodium hydroxide treated oil and withdrawn from the system by means of line 23.

The process of the present invention may be widely varied. The operation essentially comprises removing mercaptan compounds from petroleum oils, particularly from petroleum oils boiling in the general range from about 100° F. to about 425° F., utilizing an alkali metal hydroxide contacting stage and a bauxite contacting stage. Although the entire quantity of the oil may be initially contacted with an alkali metal hydroxide solution and then contacted with the bauxite, it is preferred to initially segregate a relatively low boiling fraction and a relatively high boiling fraction. In general, the relatively low boiling fraction should boil in the range from about 100° F. to about 225° F. while the relatively high boiling fraction should boil in the general range from about 200° F. to about 400° F. or about 425° F.

The alkali metal hydroxide may comprise a sodium hydroxide solution or a potassium hydroxide solution. In general, it is preferred to use a sodium hydroxide solution having a concentration in the range from about 10° Bé. to about 15° Bé. sodium hydroxide. The amount of sodium hydroxide solution employed per volume of oil will depend upon the concentration of the sodium hydroxide solution and upon the general character of the oil. When treating a petroleum oil boiling in the range from about 100° F. to about 212° F., it is preferred that 5% to 25% of sodium hydroxide solution having a 10 Bé. concentration of sodium hydroxide be utilized. Although the temperatures and pressures may be varied somewhat, it is preferred that the temperature be in the range from about 70° F. to about 80° F. and that the pressure be sufficient in order to prevent any appreciable loss of the relatively low boiling hydrocarbons.

The bauxite preferably comprises a native aluminum hydroxide containing from 50% to 70% of Al_2O_3 and from 25% to 30% of water. In general, it is preferred that the bauxite be activated by burning the same at a temperature in the range from about 500° F. to about 900° F., preferably at a temperature in the range from about 600° F. to about 800° F. The feed rates may vary considerably depending upon the general operating conditions, the character of the feed oil being treated, as well as upon the type of bauxite employed. In general, the feed rates are in the range from about 1 volume to about 7 volumes of oil per volume of bauxite per hour. The preferred rates are from about 2 to about 4 volumes of oil per volume of bauxite per hour. The bauxite also may be any desired particle size. I have found that powdered bauxite is desirable. However, the

bauxite may be utilized in the form of a slurry and the process adapted therefor.

In order to further illustrate my invention, the following example is given which should not be construed as limiting the same in any manner whatsoever.

Petroleum hydrocarbon fractions boiling in the range below about 400° F. were sweetened using a number of operations. In one operation the oil was treated with a 10° Bé. sodium hydroxide solution. In another operation the oil was treated in accordance with the process of the present invention. The results of these operations are as follows:

	Untreated oil	Operation I: Oil, extracted countercurrently in 8 stages with 20 vol. % of 10° Bé. NaOH	Operation II: Oil, filtered thru bauxite 1 v./v./hr. 100 vol. naphtha thru 1 vol. bauxite
Inspection of Oil:			
Doctor test	D. N. P.	D. N. P.	Pass
Mercaptan S, percent	0.030	0.012	0.000
Total S, do	0.215	0.187	0.163

From the above it is apparent that the sodium hydroxide extraction was effective in removing only approximately 60% of the mercaptan sulfur. It is also apparent that when treating the oil in accordance with the present invention a high quality product was obtained.

The caustic soda solution used in extracting mercaptans may be regenerated by stripping with steam in a countercurrent tower. If this operation be employed, the mercaptans are distilled overhead and the regenerated caustic removed from the bottom of the tower and recirculated to the treating system. If desired, water may be added to the regenerated caustic solution to replace water which may have been lost by distillation during the regeneration step.

The spent bauxite may be regenerated by steaming, by burning, or by other conventional methods. The preferable method of regenerating the bauxite comprises flooding the reactor with water which will displace mercaptan-containing oil from the contact mass. Following this step, the catalyst is steamed and may be heated to elevated temperatures in the range of 1000° F. to 1400° F. with the introduction of sufficient oxygen to burn any carbonaceous material remaining in the contact mass.

What I claim as new and wish to protect by Letters Patent is:

1. Process for the removal of mercaptan compounds from petroleum oils which comprises segregating a petroleum oil into a relatively low boiling fraction and into a relatively high boiling fraction in an initial stage, contacting said relatively low boiling fraction in a secondary stage with an alkali metal hydroxide solution, contacting said relatively high boiling fraction in a tertiary stage with bauxite, then combining the alkali metal hydroxide contacted oil and the bauxite contacted oil.

2. Process as defined by claim 1 in which said petroleum oil boils in the range from about 100° F. to about 425° F., in which said relatively low boiling fraction boils in the range from about 100° F. to about 225° F. and in which said relatively high boiling fraction boils in the range from about 200° F. to about 425° F.

3. A process as defined by claim 1 in which said alkali metal hydroxide solution comprises a sodium hydroxide solution having a concentration in the range from about 10° Bé. to about 15° Bé.

AMIOT P. HEWLETT.